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Disperse systems based on vegetal phosphatides

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The work investigated the alternative sources of vegetable origin, particularly fusis and hydrofusis received by sunflower and rapeseed oil purification. By the physicochemical analysis is shown the synergistic strengthen of their practically important properties as active additives, possibility for preparation of emulsions and emulsion–suspension systems with unusual micellar structure, adjustable stability, surface-active and rheological properties in a wide range of densities. Demonstrated the applications of the developed disperse systems for improving the effectiveness of disclosure productive formations, prevention of the bottomhole zone watering, completion of construction and repair of wells in conditions of abnormal formation pressures.

Currently urbanization of society and industrial human activity aimed at its achievement reached such an extent that further industrial-consumer exploitation of natural resources became dangerous for existence of humanity itself. In accordance with Declaration of 2nd UN Conference on environment and sustainable development (Rio de Janeiro, 1992), the main concepts of which confirmed and developed by world community at the summit of heads of state in Johannesburg in 2002, reasonable settlement to solve ecological-economic contradiction should be effected in parity equity with the greatest industrial, ecological and economic effectiveness. In this connection the rational usage of natural resources has to be based on non-depleting usage of renewable resources, maximum possible reduction of consumption of nonrenewable resources and extended usage of secondary resources, maximum utilization, safe rendering harmless and waste disposal, development of appropriate state-of-art technologies for these purposes.

Based on these fundamental principles, in order to receive emulsions with various practical applications we've analyzed the possibility to reduce consumption of hydrocarbon raw materials and products of its processing by rational usage of secondary products with maximum waste utilization from oil refineries and agricultural product processing enterprises [1–3].

In particular, through modification of high-tonnage acid tars highly stable emulsions being inhibitors of corrosion of oil-and-gas fields equipment were received. Based on waste of production of detergent-dispersant addition agents for lubricants and acidic waters received from production of synthetic fatty acids, highly effective invert dispersion (additive "Disine") was created – a concentrate for numerous invert-emulsion systems for oil- and gas- producing industry [2, 3].

Low biodegradability of oil-base products and increased requirements to ecological safety of used compositions promoted search and development of new ecologically safe emulsions. Comprehensive analysis of condition and evaluation of prospects to arrange their production certify necessity of complex approach to create modern technological compositions taking into account availability, cost and technological effectiveness. In our opinion, the most prospective way to resolve this task is usage of renewable agricultural resources and by-products of its processing [1, 2]. Among them high-tonnage highly-concentrated emulsions attract attention – in particular alkali soap discharges, sediment tank fuses and aquation gels (hydrofusis) which are generated by refinery of sunflower oil on oil-extracting process.

Currently soap discharges are totally used by soap industry for soap production, however fusis and hydrofusis still remain little-studied and are not used with proper application. Therefore the subject of this work was to study composition and properties of hydrofusis in order to receive emulsions and emulsion-suspension systems with regulated stability and colloidal-chemical properties.

Experimental results

Fusis used in this study is a composition of water emulsion (2,5–40 %) in vegetable oil (45–85 %) with a small quantity of substances insoluble in diethyl ether (particles of peelings, scraps of cell walls, etc. -1,5-2,5 %) and is stabilized with phosphatides (10–45 %).

Hydrofusis represent oil emulsion (10–30 %) in water (40–70 %) stabilized with phosphatides (20–45 %). Solid light grey residue prepared by vacuum drying reminds walnuts by taste and has a smell of sunflower oil. For analysis of their composition, water was separated from hydrofusis with acetone extraction. A residue was separated, dried up and divided into fractions by dissolution in ethanol. Cephalin fraction was filtered (24 %) and ethanol solution was evaporated to yield lecithin (18 %).

In order to analyze interaction of phosphatides with solvents and determination of their molecular affinity to phases with different polarity, we have carried out systematic studies of solubility of primary mixture of phosphatides and separated fractions in oils and hydrocarbons. As nonpolar solvents there were used pure hydrocarbons with various content of carbon atoms (octane, decane, hexadecane) and their technical mixtures (diesel fuel, gas condensate). It was found that with increase of molecular mass, viscosity and density of used hydrocarbons the intermolecular interaction between phosphatides and a solvent is also increased that results in rise of dispersion's viscosity in order: diesel fuel < hexadecane < decane < octane. Addition of polar solvents, for example, water, promotes transfer of hydrocarbon solutions of phosphatides into gel state due to transformation of spherical invert micelles to cylindrical ones and structuring of a whole system.

Having used received regularities of changes in properties of fusis and hydrofusis in various solvents, we've obtained direct and invert emulsions and emulsion– suspension systems with regulated properties and stability. Composition of prepared dispersions and results of systematic analyses of their colloidal-chemical properties is given in the table.

Emulsion–suspension systems were prepared by addition of solid bulking agent to the corresponding fine emulsions such as barium sulfate (BaSO₄) with a specific gravity $\rho = 4500 \text{ kg/m}^3$, calcium carbonate (CaCO₃) with $\rho = 2710 \text{ kg/m}^3$, gas-filled or solid glass microspheres. The latter are regular spheres of sodium–boron–silicate glass with $\rho =$ $= 2400 \text{ kg/m}^3$. Gas-filled microspheres are free flowing powders which formed from thin wall (0,5–2,0 microns) glass particles in the correct spherical shape with a diameter $10-180 \text{ }\mu\text{m}$ and a specific gravity of 265–280 kg/m³.

Discussion

It was found that hydrofusis and their components – lecithin, cephalin – can be dissolved in many hydrocarbonic and organic solvents – heptane, octane, nonane, decane, chloroform, benzene, toluene, carbon tetrachloride, tetrahydrofuran, diethyl ether, petroleum ether, etc. They can be dissolved little bit less in tetradecane, hexadecane, gas condensate, diesel fuel. Unlike cephalin, lecithin can be dissolved well in diethyl ether and isopropyl alcohol. In methyl acetate, acetone and other ethers and ketones both compounds, like hydrofusis itself, can not be dissolved even at heating. In acid and alkali conditions a disintegration of phosphatides is observed with generation of dispersions of milky colour.

It is established that, unlike fats, phosphatides of vegetal oils have properties of hydrophilic colloids. In the presence of water they swell that is induced with hydrolysis of salt state group and transfer to a form where free hydroxyls are present.

In industrial conditions at processing of raw oil with water vapours at pressure of $2-3 \cdot 10^5$ Pa due to aquation of hydroxyls the pasty water-in-oil emulsions are formed. When they are diluted with water, due to reduction in concentration of phosphatides, structure of the system is changed and emulsions come to fluid condition forming opalescent blurred systems. Received emulsions at mild temperatures (up to 60 °C) are stable in time. With increase of water content, as seen from sample 1–3, (see the table), viscosity of emulsions is reduced and density is increased.

The presence in molecules of bulky hydrophilic part generated by polar groups of phosphoric acid and nitrogen basis enables phospholipids to disperse in water whereas hydrophobic radicals from long aliphatic chains – residues of higher saturated and unsaturated acids – impart them an affinity to organic solvents. By tendency to hydration, individual groups of oil phospholipids are arranged in the following order: phosphatide acids < phosphatidyl ethanolamines < phosphatidyl cholines. High hydration level of phosphatidyl cholines is caused by simultaneous presence in molecule of acid and basic groups due to which in water they almost entirely come to ionic form to form zwitterions.

Unlike phosphatidyl ethanolamines and phosphatidyl inositols a higher hydration of lecithins is caused by absence in their molecules of intermolecular hydrogen bonds which prevents the water penetration to polar groups of phospholipids. Due to this fact, all analyzed phosphatides give colloidal solutions of certain level of dispersion both in hydrocarbons and water. This process proceeds through swelling of phosphatides with creation of lamellar anisotropic melt. At mechanical influence, for example, by ordinary shaking or mixing with mechanical mixers, dispersing of swelled mass in excess of solvent takes place with formation of closed lamellas named vesicles [4]. At higher concentrations multilamellar vesicles are easily formed with diameter of particle from 0,1 till 100 µm. Generated paste-like mass has pseudoisotropic texture with oil furrows.

In organic solvents phospholipids form spherical micelles but at specific concentration of surfactants and in low quantity of water they swell generating viscous gel state emulsions. With increase of concentration to 5-7 % molecules of phosphatides are lengthened and transformed into cylindrical units. An increase of viscosity after addition of water is proved to be stipulated by univariate growth and generation of huge rod-like micelles which interlace and form in volume three-dimensional grid similar by flow properties semidiluted solutions of polymers rather than swelled associates of molecules.

Addition into organic solutions of phospholipids of polar solvents (water, dimethyl formamide, glycol) promotes generation of jellous structures with high level of structuring in volume by hydrogen bonds. Phosphatides are bonded with water molecules by four hydrogen bonds. Binding of solvents by phosphatides in organic gels is proved by spectral studies. As for IR spectra, the most intensity has v (C=O) absorption band. After addition of solvents its maximum practically remains at 1715 cm⁻¹. Perceptible shift to absorption of C–O–C ester groups is not observed. This fact witnesses for absence or not strong enough influence of polar solvents with carbonyl groups and glycerine residue of phospholipid molecules. Nevertheless, important shifts are observed for absorption zones of phosphate

| <u>№№</u> Sam- | Nº№ Aqueous Sam- % vo | | C | Oil fase, % vol. | | Phopha- tides, | Additives, % vol. | | Emulsion`s type, consistency | Density, kg/m ³ | Viscosity, Pa·c | Electrical- stability, | Separation of hydrocarbon, |
|-------------------|--------------------------|---------------|-------|------------------|-----------------|-------------------|-------------------|--------|---------------------------------|-------------------------------|--------------------|---------------------------|----------------------------|
| ples | Solubi- lizat. | Addi- tion | Oil | Diesel fule | Conden- sate | % vol. | Title | Amount | | ng m | Tae | V V | % vol./day |
| 1 | 50,00 | _ | 22,00 | _ | _ | 28,00 | _ | _ | o/w, paste | 980 | >4,0 | _ | 0 |
| 2 | 27,50 | 45,00 | 12,10 | _ | _ | 15,40 | - | - | o/w, low flowing | 990 | 0,70 | _ | 0 |
| 3 | 22,10 | 54,50 | 9,70 | 1,30 | _ | 12,40 | _ | _ | o/w, low flowing | 980 | 0,45 | _ | 0 |
| 4 | 35,00 | 28,30 | 15,20 | 2,00 | _ | 19,50 | _ | _ | o/w, moving system | 970 | 1,50 | _ | 0 |
| 5 | 47,90 | _ | 21,10 | 4,20 | _ | 26,80 | _ | _ | w/o, paste | 960 | >4,0 | _ | 0 |
| 6 | 46,10 | _ | 20,30 | 7,80 | _ | 25,80 | _ | _ | w/o, paste | 950 | >4,0 | _ | 0 |
| 7 | 38,60 | _ | 17,00 | 22,80 | _ | 21,60 | - | _ | w/o, paste | 940 | >4,0 | _ | 0 |
| 8 | 35,30 | _ | 15,50 | 29,40 | _ | 19,80 | - | _ | w/o, moving system | 930 | 0,52 | >500 | 0 |
| 9 | 31,20 | _ | 13,80 | 37,50 | _ | 17,50 | _ | _ | w/o, low flowing | 920 | 0,26 | >500 | 0 |
| 10 | 17,80 | 42,90 | 7,80 | 21,50 | _ | 10,00 | _ | - | w/o, plastic system | 950 | 3,10 | 220 | 0 |
| 11 | 20,70 | 53,90 | 9,30 | 4,50 | _ | 11,60 | _ | _ | w/o, paste | 860 | >4,0 | — | 0 |
| 12 | 16,20 | 64,70 | 7,20 | 2,90 | I | 9,00 | - | - | w/o, paste | 894 | >4,0 | — | 0 |
| 13 | 11,40 | 75,60 | 5,00 | 1,10 | I | 6,90 | - | - | w/o, paste | 920 | >4,0 | — | 0 |
| 14 | 36,00 | - | 47,00 | _ | _ | 17,00 | - | _ | w/o, low flowing | 950 | 0,67 | - | 2 |
| 15 | 25,70 | 28,60 | 33,60 | _ | _ | 12,10 | - | - | w/o, low flowing | 966 | 0,72 | - | 0 |
| 16 | 18,50 | 47,80 | 24,75 | _ | _ | 8,95 | - | _ | w/o, low flowing | 975 | 0,94 | - | 0 |
| 17 | 18,00 | 50,00 | 23,50 | _ | _ | 8,50 | _ | _ | o/w, easy flowing | 976 | 0,45 | _ | 0 |
| 18 | 7,20 | 80,00 | 9,40 | _ | _ | 3,40 | - | _ | o/w, flowing | 990 | 0,007 | _ | 70 (water) |
| 19 | 7,00 | 78,60 | 9,20 | _ | _ | 3,30 | bentonit clay | 1,90 | o/w, flowing | 980 | 0,009 | _ | 0 |
| 20 | 17,80 | 26,95 | 7,80 | _ | 36,95 | 10,00 | emultal | 0,5 | w/o, moving system | 900 | 2,20 | >500 | 2 |
| 21 | 9,00 | 38,20 | 3,90 | _ | 43,40 | 5,00 | emultal | 0,5 | w/o, flowing | 890 | 0,09 | >500 | 4 |
| 22 | 5,50 | 50,00 | 2,42 | _ | 37,58 | 3,00 | emultal | 1,5 | w/o, moving system | 910 | 1,28 | 150 | 2 |
| 23 | 9,80 | 37,45 | 4,30 | 42,95 | _ | 5,50 | _ | _ | w/o, moving system | 925 | 0,055 | 330 | 3 |

| Composition and properties emulsions on the basic phosphatides of vegetable oil | 5 |
|---|---|
|---|---|

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Table continued

| <u>№№</u> Sam- | Aqueous fase, % vol. | | C | Oil fase, % vol. | | Phospha- tides, | Additives, % vol. | | Emulsion`s type, consistency | Density, kg/m ³ | Viscosity, Pa·c | Electrical- stability, V | Separation of hydrocarbon, |
|-------------------|-------------------------|-----------------------------------|-------|------------------|-----------------|--------------------|--|-----------------|---------------------------------|-------------------------------|--------------------|-----------------------------|----------------------------|
| ples | Solubi- lizat. | Addi- tion | Oil | Diesel fule | Conden- sate | % vol. | Title | Amount | | - | | | % vol./day |
| 24 | 31,70 | 9,40 | 13,90 | 27,20 | - | 17,80 | - | - | w/o, plastic system | 930 | 3,70 | >500 | 0 |
| 25 | 17,00 | 30,00 | 8,00 | _ | 35,00 | 10,00 | _ | _ | w/o, plastic system | 900 | 2,20 | >500 | 4 |
| 26 | 13,60 | 45,00 | 6,00 | _ | 27,70 | 7,70 | _ | _ | w/o, plastic system | 910 | 3,20 | 420 | 3 |
| 27 | 6,25 | 50,00 | 2,50 | _ | 37,75 | 3,50 | _ | _ | w/o, flowing | 907 | 0,80 | 100 | 3 |
| 28 | 4,21 | 26,80 | 1,84 | _ | 55,70 | 2,35 | CaCO ₃ | 9,10 | w/o, flowing | 1020 | 0,05 | 220 | 10 |
| 29 | 3,85 | 25,00 | 1,70 | _ | 51,00 | 2,15 | CaCO ₃ | 16,30 | w/o, moving system | 1170 | 0,12 | 230 | 8 |
| 30 | 3,50 | 22,70 | 1,50 | - | 47,2 | 2,00 | CaCO ₃ | 23,10 | w/o, moving system | 1280 | 0,25 | 240 | 7 |
| 31 | 5,00 | 25,50 | 6,60 | _ | 51,42 | 2,38 | BaSO ₄ | 9,10 | w/o, flowing | 1200 | 0,07 | 190 | 10 |
| 32 | 4,60 | 23,80 | 6,00 | - | 47,20 | 2,10 | BaSO ₄ | 16,30 | w/o, moving system | 1450 | 0,36 | 200 | 7 |
| 33 | 4,20 | 21,60 | 5,50 | _ | 43,60 | 2,00 | BaSO ₄ | 23,10 | w/o, moving system | 1700 | 0,44 | 210 | 6 |
| 34 | _ | 15,40 38% CaCl ₂ | 2,20 | 26,43 | _ | 3,20 | CaCO ₃ , Microsphere $(\rho=2400 \text{ kg/m}^3)$ | 14,02, 39,05 | w/o, moving system | 1740 | | >500 | 2 |
| 35 | _ | 39,20 10% CaCl ₂ | 3,45 | 29,49 | _ | 3,45 | Microsphere (ρ=265κg/m ³) | 24,41 | w/o, moving system | 770 | 0,24 | 190 | 5 |
| 36 | _ | 18,50 10% CaCl ₂ | 4,80 | 20,70 | _ | 6,20 | Microsphere $(\rho=280 \text{ kg/m}^3)$ | 49,80 | w/o, plastic system | 610 | 1,36 | 235 | 0 |
| 37 | _ | 25,98 Н ₂ О | 2,02 | 18,08 | _ | 5,60 | Microsphere $(\rho=280 \text{ kg/m}^3)$ | 48,32 | w/o, moving system | 530 | 0,69 | 330 | 4 |

group. Maximum v (P=O) absorption band is shifted from 1265 to 1220 cm⁻¹. This shift Δv is induced by generation of hydrogen bonds with formation of which the gel state structure is explained [5, 6]. Hydration of P=O groups and reduction of frequency orientation caused by it certify that phosphatide group is the most favourable place to connect water molecules. Namely due to that the latter has the biggest polarity and both donor (P–OH) and acceptor (P=O) centers which participate in generation of hydrogen bonding, the group is enable to form heteromolecular associates similarly to gel forming solvents. With increase of water concentration till certain critical parameter, when water acts as thickening agent, not only viscosity is increased, but also density of emulsions whereas system stability is slightly reduced.

Similar changes are observed when to add to direct emulsions small quantity pure hydrocarbon solvents (hexane, heptane, octane, nonane, decane), gas condensate, oil, diesel fuel and other oil products. Contrary to colloidal dissolution of water in organic gels [4], in hydrofusis stabilization of hydrocarbons is observed that is accompanied also by intensive increase of viscosity (samples 2-4) till transfer of the system to stagnant pasty condition (samples 5–7). Increase of concentration of diesel fuel till 4,2 % results in phases conversion with formation of inverse emulsions w/o (sample 5) which by properties are complete opposition to the previous ones. Samples of emulsions 5–9 indicate that diesel fuel reduces density of primary invert emulsions increasing plasticity of stagnant mass right up to its transformation to mobile system (sample 8) and further - to fluid low viscous invert emulsion (sample 9) with maximum electrical stability and high sediment stability. Additional introduction of water into mobile systems causes increase of their viscosity and transfer to paste state (samples 10-13). Electrical stability is deteriorated for the last three samples due to high content of water phase (more then 60 %). On the contrary, sediment stability of emulsions owing to high viscosity remains sufficient even at heating till 100 °C. Also our attention attracts the fact that after adding large quantity of water to emulsion w/o (till 87 %), despite small quantity of diesel fuel (1,1-4,5 %), the system remains inverse and stable (sample 13).

In the area of transitional ratios of water/hydrocarbon an increase of viscosity of systems occurs till certain critical content both water and hydrocarbons. Above this level stipulated by peculiarities of micelles structures, semisolid mass with maximum quantity of water hold by hydrophilic layers of vesicles "rolls" in surplus of water without phase inversion due to significant energy consumption on destruction of created structure. Interestingly that in transitional area when hydrocarbons are added, systems are also thick-ened into semisolid mass with further increasing plasticity of emulsions w/o (samples 5–7) and their transfer to fluid liquids (samples 8–9). These emulsions are stable in time owing to high association and structuring of phosphatide molecules in a volume.

Unlike hydrofusis of vegetal oils that are emulsions o/w, fusis are stable emulsions w/o. Containing phosphatides and high oil content are favourable for creation of inverse structures in which contained water is in colloidal dissolved state (sample 14). Added water is not solubilized now but emulsified with formation of stable emulsions as seen from table (samples 15-16). Whereas stability and viscosity of emulsions naturally increases with increase of water concentration that confirms convincing formation of inverse emulsions exactly. Probably, phosphatides form threedimensional grid by hydrogen bonding. As consequence viscosity increases reaching maximum in the region of 64,3 % water content. Further water addition changes water-oil ratio to formation of hydrophilic systems that results in phases inversion and emulsions w/o change into o/w emulsions. The viscosity falls sharply what is observed in examples 17 and 18. Probably, when nature of dispersion environment is changed to polar solvent - water, internal hydrophobic core consolidates and highly hydrate shell is formed around functional hydrophilic groups of phosphatides which increases effective cut space of polar areas and promotes conversion of hexagonal anisotropic melt to lamellar one.

Unlike hydrofusis, which emulsions remain stable in all the range of ingredient ratios, irrespective of type of vegetal oils (samples 14–17), emulsion systems based on fusis at increased water content are already unstable. For example, when water content is higher then 87 % (sample 18), coagulation of phosphatides is observed that is water acts as flocculant. Consequently, determinative criteria of emulsions stability is both a concentration of active substance and a ratio of mutually not soluble phases - water and oil. Just optimal correlation ensures stability of right emulsions and presents the most important lever to control disperse system properties on basis of phosphatides of vegetal oils. When quantity of phosphatides is sufficient, consistence and viscosity of invert emulsions are easy to regulate at each stage of preparation keeping principle necessary condition: in case of increased viscosity the oil phase is added to the system in order to reach of necessary parameters, whereas for thickening of emulsions an additional quantity of water or water solution is introduced into.

It should be noted that majority of received emulsions is not only sedimentary stable within prolonged period of time but thermally stable in wide temperature interval. In particular, it is shown that a sample, which corresponds to content 19, remains homogenous at constant ageing in thermostat in range of temperatures of 20–95 °C during 3 days. Structuring and high stability of emulsions are confirmed by results of filtration studies.

Regulation of properties of obtained invert emulsions is possible also by introduction of known emulsifiersstabilizers, solutions of mineral salts and weighting materials. Additional introduction of surfactants, for example emultal, facilitates preparation, reduces duration of agitation, increases stability of invert emulsions at reduction of concentration of phosphatides and considerable improves technological properties (samples 20–22) what considerably improves technical-economical and ecological indices of emulsion usage.

Properties of emulsions for samples 23–24 indicate that at equal volume ratio of water and hydrocarbon phases with increase of phosphatides concentration from 5,5 % till 17,8 %, consistence changes and viscosity increases with preservation of high sedimentary stability. By reducing phosphatides concentration from 10,0 % till 7,7 % and increasing concentration of water phase from 47 % to 59 % viscosity of emulsions as in previous cases (samples 9–10) is increased (samples 25–26). For sample 27 quite low values of viscosity and electrical stability are typical that is provided by low content of phosphatides. Consequently, necessary condition to improve properties of analyzed emulsions is increase of phosphatides concentration or additional introduction of co-detergents like emultal (samples 20–22).

Studies of system's stability have shown that direct emulsions with concentration of fillers 10-30 % are stable only at o/w ratio equal to 0,1/0,9, concentration of phosphatides more then 4 % and temperature not exceeding 60 °C. Under other conditions, owing to insufficient volumetrical filling of systems and low adherence, adsorptionsolvate layer on surface of drops of hydrocarbon and solid phases formed by phosphatides appears to be very weak and is destroyed partially generating suppositions to flocculation of internal phase and exfoliation of emulsions. The temperature intensifies this factor and renders assistance to accelerate exfoliation process. It is established also that prevention of exfoliation and rise of stability of w/o emulsions stabilized by phosphatides can be achieved by introduction of gel-forming agents, for example, bentonite clay (sample 19) or fine-dispersed fillers (calcium carbonate, barium sulfate) or attendant surface active fillers (oxyethylated alkylphenols – neonols AF₉-10 and AF₉-12), synthetic fatty acids with fractions C₁₂₋₁₄, mixtures of tars of vegetal fats and adiposis which are generated in the result of distillation of fat acids from soap stock of vegetal oils or adiposis, and mixtures of complex alkylol amides obtained by their interaction with ethanol amines. In these cases, viscosity end density of w/o emulsions increases in proportion to concentration of added water.

W/o Emulsions are very stable without additional stabilizers due to interaction of primary monolayer of redially oriented bulky hydrophilic groups of phospholipids with surface of drops of internal water phase intensifies interaction of unsaturated hydrocarbon chains of oleic, linolenic and other polyene acids, and together with hydrocarbon radicals of saturated fatty acids provides not only affinity of micelle structures with hydrocarbon environment but secures also long-distance component of systems order and its effective structuring. No doubts, this is assisted to generate multilayer vesicles which divide water drops and particles of solid phase and prevent their coalescence. This confirms convincingly changing of type of emulsions from direct emulsion to invert one owing to intensive mixing of dispersions and insignificant increase of concentration of hydrocarbon phase (samples 5, 11-13).

Based on broad physical-chemical studies of hydrofusis by synergetic intensification of practically important properties with active additives of highly dispersed fillers, we've received a number of invert emulsion–suspension systems with regulated stability, surface active and rheological properties in broad range of density – from 530 till 1740 kg/m³.

In order to reduce density of emulsion-suspension systems the filled with gas microspheres with high mechanical solidity and density of 265–280 kg/m³ were added to them. Microspheres are slightly moistened with water and organic solvents therefore their introduction into system should be realized by special technology keeping with certain correlation of water and hydrocarbon phases with sufficient quantity of emulsifier. In the systems with a high content of aqueous phase (correlation water/hydrocarbon = 70,0/30,0), despite large concentration of phosphatides (> 17 %), owing to high viscosity it's possible to introduce not more than 20 % of microspheres. On the contrary, by increase of content of hydrocarbon phase till 25 % with considerably lower concentration of phosphatides (3,5-6,2 %) we've received fluid emulsion in which it is possible to introduce up to 50 % of microspheres (samples 28-30). With further increase of microspheres concentration the systems again lose mobility and become paste state. Presumably, despite large difference in specific gravity of dispersion system and filler due to forming of three-dimensional cellular system by phosphatides mentioned above, emulsion-suspension systems remain highly structured and easily prevent microspheres from separation.

Density increase is easily achieved by addition to emulsions of typical weighting materials – $CaCO_3$ (samples 31– -33) and $BaSO_4$ (samples 34–36), and also solid glass microsphere (sample 37). Whereas their introduction doesn't deteriorate properties of systems but renders emulsions structuring and reduction of filtration. Increase of quantity of solid phase results in increase of both density and viscosity even when concentration of phosphatides is not high.

Summing up complex research results on structure and properties of compositions on the basis of vegetable phosphatides it can be argued that due to an unusual structural organization, low interfacial tension, high solubilized ability to both polar and non-polar solvents, it was succeeded to develop ways of structure regulation of disperse systems. On this basis created reagent for inverse emulsions [7], which is used in the development of a number of practically important dispersed compositions [8]. We propose stable emulsion–suspension systems for the completion of the construction and repair of wells in conditions of abnormal formation pressures [9, 10]. Further research of the regularities of self-organization of the phosphatides in environment of different polarity and development of ideas about changing the nature of wetting breed of bottomhole zone were allowed to develop effective structures for tapping of productive formations, prevention of watering [11], decolmatation and improve the efficiency of oil, gas and gascondensate wells [12].

Conclusions

1. Phosphatides of vegetal oils are characterized by increased solubilization, surface activity and related to them strongly pronounced emulsifying and stabilizing properties. Viscosity and stability of their emulsions increase with increase of phosphatides concentration.

2. In dispersion systems based on phosphatides of vegetal oils water plays role of builder and stabilizer. Increase of quantity of added water increases viscosity and stability of invert emulsions.

3. When quantity of phosphatides is sufficient, consistence and rheological properties of emulsions are easily to regulate at every stage of preparation by adding water or hydrocarbons. Viscosity of emulsions changes from fluid, easy mobile with regulated stability to semisolid paste state systems by change of water/hydrocarbon phases ratio.

4. Owing to insignificant volume filling of hydrophilic systems and low adhesion of surface active substances, the adsorption-solvate layer formed by phosphatides and water on surface of drops of oil phase is destroyed. The presence of small quantity of hydrocarbon solvent phases is lead to inversion with generation of stable w/o emulsions stabilized by mixed monolayer of emulsifier. The acyl residues of emulsifier are provided for connection of micelle structures with hydrocarbon environment and increased structuralmechanic properties of generated dispersion systems.

5. Emultal addition as co-detergent facilitates preparation, reduces time of mixing and increases stability of invert emulsions when concentration of phosphatides is reduced what improves technical-economic and ecological characteristics of usage of emulsions.

6. Introduction to emulsions of known weighting agents – CaCO₃, BaSO₄, glass microspheres – allows to increase their density up to 1740 kg/m³ providing whereas high stability of systems. Filling of emulsions stabilized by phosphatides with gas microspheres reduces their density till 510 kg/m³ whereas systems remain stable within long period of time.

7. Owing to possibility to regulate colloidal-chemical

properties and stability in wide range of water/oil phases ratio, concentrations of vegetable phosphatides and codetergents, active additions of mineral salts, fillers and clays, invert emulsions can be widely applied in gas-and-oil production industry as technological liquids for tapping of productive formations, prevention of watering, completion of construction and thorough repairs of wells.

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Дисперсні системи на основі рослинних фосфатидів

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В роботі досліджені альтернативні джерела рослинного походження, зокрема фузи і гідрофузи від очистки соняшникової та ріпакової олій. На основі фізико-хімічних досліджень та синергетичного підсилення їх практично-важливих властивостей активними добавками показана можливість отримання емульсій та емульсійно-суспензійних систем з незвичайною міцелярною структурою, регульованими стабільністю, поверхнево-активними і реологічними властивостями в широкому діапазоні густини. Продемонстрована можливість використання розроблених дисперсних систем для підвищення ефективності розкриття продуктивних пластів, попередження обводнення привибійної зони, завершення будівництва та ремонту свердловин в умовах аномальних пластових тисків.

Дисперсные системы на основе растительных фосфатидов

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В роботе исследованы альтернативные источники растительного происхождения, в частности фузы и гидрофузы от очистки подсолнечного и рапсового масла. На основе физикохимических исследований и синергетического усиления их практически-важных свойств активными добавками показана возможность получения эмульсий и эмульсионносуспензионных систем с необычной мицеллярной структурой, регулируемыми стабильностью, поверхностно-активными и реологическими свойствами в широком диапазоне плотностей. Продемонстрирована возможность использования разработанных дисперсных систем для повышения эффективности раскрытия продуктивных пластов, предупреждения обводнения призабойной зоны, завершения строительства и ремонта скважин в условиях аномальных пластовых давлений.